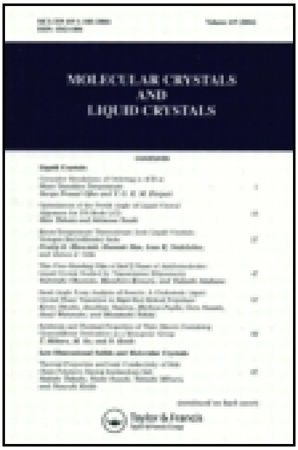

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Design of TiO 2 /Activated Carbon Fiber Systems by An Ionized Cluster Beam Method and Their Application for the Photocatalytic Water Purification

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DESIGN OF TiO_2/ACTIVATED CARBON FIBER SYSTEMS BY AN IONIZED CLUSTER BEAM METHOD AND THEIR APPLICATION FOR THE PHOTOCATALYTIC WATER PURIFICATION

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Preparation of titanium oxide photocatalysts loaded on activated carbon fiber (ACF) using an ionized cluster beam (ICB) method and their photocatalytic reactivity for the water purification, the oxidative degradation of organic pollutants (alkyl alcohols, dichloroethane) diluted in water, was investigated. The utilization of the ICB method under oxygen atmosphere enables the preparation of titanium oxide photocatalysts on ACF relatively low temperature without causing any damages to the supports. Characterization using spectroscopic techniques indicates that fine particles of TiO_2 are formed on the supports mainly as an anatase structure. The combination of the photocatalytic reactivity of TiO_2 and the adsorption ability of ACF was effective for the degradation of oraganic pollutants diluted in water into CO_2 , H_2O and HCl.

Keywords: activated carbon fiber; ionized cluster beam method; photocatalysis; titanium oxide; water purification

INTRODUCTION

The photocatalytic degradation of organic toxic compounds dissolved in water using photocatalysts has attached a great deal of attention [1,2]. For this purpose, the design of TiO_2 photocatalysts on activated carbon fibers (ACF) which have large surface areas and can condense diluted toxic compounds is attractive to achieve highly efficient photocatalytic systems [3–8]. Although the use of activated carbons or activated carbon fibers as catalyst supports had been reported [3–8], they are easily damaged in oxygen at around 500 K, the temperature which is required to prepare titanium oxide microcrystals on these supports by conventional

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preparation methods such as impregnation and dip coating. “Ionized cluster beam (ICB) method” has been shown to be one of the most useful techniques in preparing metal oxide thin films or clusters loaded on various types of supports under mild and dry conditions [4–8]. In this study, we have applied this advanced technique to develop TiO_2/ACF at relatively low temperature and made the successful utilization of these systems for the oxidative degradation of organic compounds diluted in water.

EXPERIMENTAL

Titanium oxide catalysts loaded on felt (20 × 30 × 5 mm, ~70 mg) of ACF (Toho Rayon Co., FX-300, 900 m^2/g) were prepared by the ICB method using a Ti metal as the source material under a dilute O_2 atmosphere. A systematic diagram of the ICB method is shown in Figure 1. The Ti cluster beam was produced by the ejection of the Ti vapor ionized by the electrons emitted from the ionization filament. The produced ionized clusters were then accelerated by an accelerating electrode. Active titanium oxide were produced by the impingement of the ionized clusters and oxygen gas onto the support substrate. In these experiments, the acceleration voltage, the substrate temperature, and the oxygen gas pressure were 0.25 kV, 523 K, and 2.0×10^{-4} Torr, respectively. The photocatalysts were then transferred into a quartz cell containing an aqueous solution of alkyl alcohols (2-propanol, 2-butanol, 2-pentanol, 2-hexanol) or 1,2-dichloroethane (2.6×10^{-3} mol/l, 25 ml) and irradiated at 295 K using UV light ($\lambda > 280$ nm) from a high-pressure Hg lamp under O_2 atmosphere. The

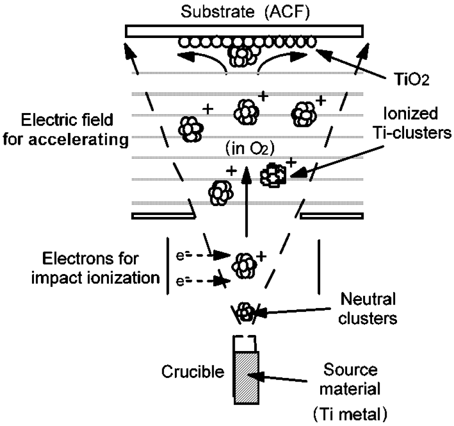

FIGURE 1 Systematic diagram of the ionized cluster beam (ICB) method.

products were analyzed by gas chromatography. The X-ray absorption fine structure (XAFS) spectra, X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), were measured at the BL-9A facility of the Photon Factory at the National Laboratory for High-Energy Physics. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K. The normalized spectra were obtained by a procedure described in previous literature [9].

RESULTS AND DISCUSSION

Characterizations of TiO_2/ACF photocatalysts prepared by the ICB method by the SEM technique showed the titanium oxides to be deposited on the ACF as small particles. The migration of the titanium ion clusters was not easy on ACF with its numerous micropores, resulting in the formation of titanium oxide fine particles and not thin films [4–6]. Figure 2 shows the XAFS spectra of TiO_2/ACF photocatalysts. From the observations of three characteristics weak preedge peaks in the XANES spectra and the observation of peaks due to the neighboring titanium atoms in the FT-EXAFS spectra indicate the presence of an octahedral coordinated titanium oxide much like crystalline anatase. With increasing the Ti contents, the crystalline phase has changed from anatase to mixture of anatase and rutile. These results are in good agreement with the results of XRD analysis.

Figure 3 shows the profiles of the photocatalytic degradation of 1,2-dichloroethane diluted in water on the TiO_2/ACF. In the initial stage of the reaction under dark conditions, the adsorption of 1,2-dichloroethane onto

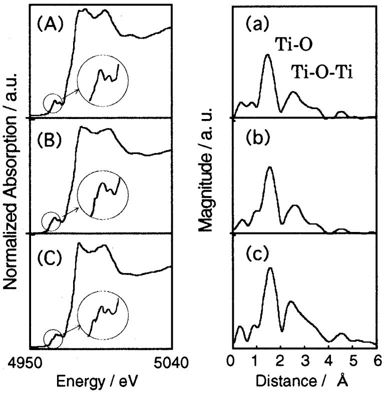

FIGURE 2 XANES and Fourier transforms of EXAFS spectra of the the TiO_2/ACF. Ti content: (A,a) 3, (B,b) 1, (C,c) 0.3 wt% as Ti. (Calcination: 523 K under air for 5 h).

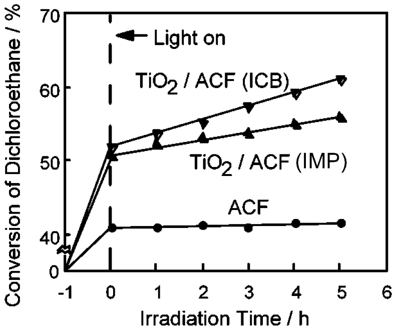

FIGURE 3 The profiles of the photocatalytic degradation of 1,2-dichloroethane diluted in water on the TiO_2/ACF prepared by the ICB method and the impregnation using an aqueous solution of $(NH_4)_2TiO(C_2O_4)_2$ (Ti content: 3 wt%, calcination: 523 K).

the photocatalysts can be observed. This process followed the Langmuir adsorption and the adsorption was saturated within 1 hour before the UV irradiation. When UV light is turned on, the 1,2-dichloroethane is decomposed finally into CO_2, H_2O and HCl under UV irradiation. The TiO_2/ACF exhibits higher photocatalytic reactivity than the catalyst prepared on ACF by the impregnation method using an aqueous solution of $(NH_4)_2TiO(C_2O_4)_2$. These results indicate that with the ICB method it is possible to prepare highly crystalline anatase TiO_2 photocatalyst at low

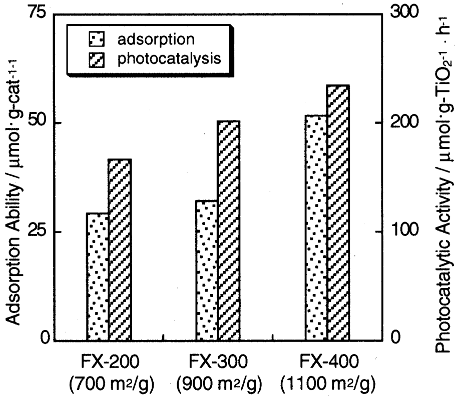

FIGURE 4 Effects of the surface area of the TiO_2/ACF prepared by the ICB method on their adsorption abilities and photocatalytic reactivities in the liquid-phase photocatalytic oxidative degradation of 2-propanol diluted in water at 295 K.

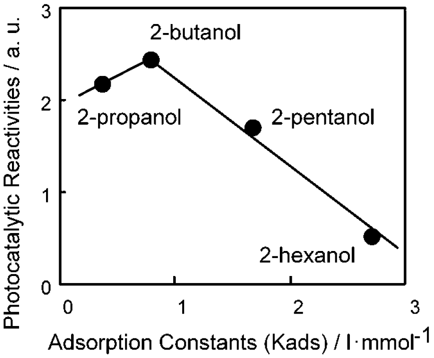

FIGURE 5 Effects of the adsorption property of ACF with the organic compound on the photocatalytic reactivity for the degradation of alcohol diluted in water on the TiO_2/ACF system (Ti content: 3 wt%, calcination: 423 K).

calcination temperatures without damaging the microporous structure of the ACF supports.

The photocatalytic degradation of 2-propanol diluted in water was also studied. Under dark conditions, the adsorption of 2-propanol onto the photocatalysts was observed. When the UV light was turned on, the 2-propanol decomposes into acetone, CO_2 and H_2O, and finally acetone was also decomposed into CO_2 and H_2O. Figure 4 shows the adsorption and photocatalytic properties of several TiO_2/ACF photocatalysts prepared with various ACF of different surface areas. The photocatalysts prepared with

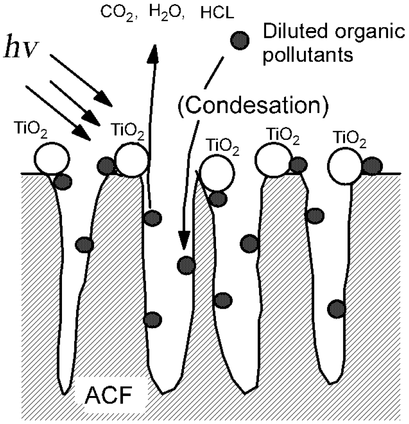

FIGURE 6 Scheme of the photocatalytic degradation of organic compounds diluted in water using TiO_2/ACF systems.

ACF having a larger surface area exhibits a higher adsorption ability and photocatalytic reactivity.

The effects of the interaction between organic compounds and ACF on the photocatalytic properties of the TiO_2/ACF have been investigated using various types of sec-alcohols. As shown in Figure 5, the efficient photocatalytic reaction proceeds on the system having the moderate interaction between ACF and organic compounds. These results indicate the combination of adsorption properties of ACF and photocatalytic reactivity of TiO_2 is essential for the realizing of the efficient photocatalytic degradation system.

CONCLUSIONS

The present results indicate that combining the superior adsorption properties of ACF and the efficient photocatalytic reactivity of TiO_2 fine particles allows the efficient degradation of organic pollutants diluted in water. By the ICB method, active TiO_2 photocatalysts can be loaded on ACF without serious damage in the adsorption properties.

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